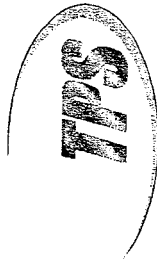




Processing and Properties of HfB₂ Based Materials

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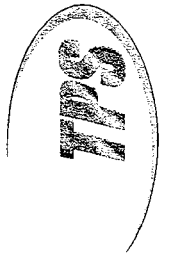




Contributors



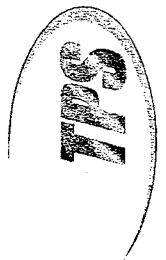
- NASA Ames Research Center
 - Ed Martinez, Tom Squire, Joe Olejniczak, Ricardo Olivares, and the Ames Arc Jet crew
- ELORET at NASA Ames Research Center
 - Jerry Ridge, Matt Switzer, Valerie Vinisko
- NASA Glenn Research Center
 - John Salem





Outline

- Background on UHTCs
 - Summary UHTC Processing
 - Powder Processing
 - Scale-up
 - 2" dia. X 2" tall billets
 - 3" dia. x 2" tall billet
- netting*
- Preliminary Material Properties
 - Mechanical
 - Thermal
 - Summary
 - Future Work

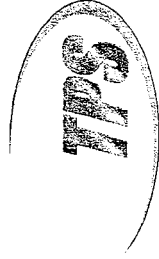




Development of Ultra High Temperature Ceramics



- UHTCs are a family of ceramic materials, including diborides of Hf and Zr, with extremely high melting temperatures
- Previous studies have indicated good oxidation resistance in simulated reentry environments
 - ManLabs 1960's and 1970's
 - ARC 1990's
 - Ground based research: initial materials development by external vendors, Arc Jet testing, computer modeling, etc.
 - SHARP-B1(1997) and SHARP-B2 (2000) ballistic flight experiments
 - » Materials provided by external vendors
 - » Different vendors used for each flight experiment
 - » Focus on flight experiment not on materials development
 - Detailed studies still required to define use environments (Single and Multi-Use Temperatures)

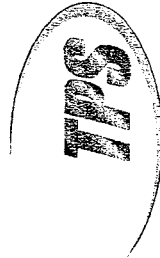




Motivation for In-House Processing of UHTC Materials



- Until now there has been no consistent effort to develop the UHTC family of materials at NASA.
 - Development work has primarily been part of flight experiment programs.
 - SHARP-B1 and SHARP-B2
- Different vendors supplied materials for the SHARP-B1 and SHARP-B2 flight experiments.
 - NASA did not retain the knowledge on how to process these materials.
 - Therefore, each time the materials development has had to start at the beginning, evaluating material properties, etc...
- Resulted in inconsistent materials
 - Significant differences in microstructure leads to significant variability in material properties.
- Bringing the UHTC processing in-house allows the government to retain the knowledge of how to process the materials and then transfer the technology to industry for production.
 - Precedent has been set at ARC with development of tile coatings.





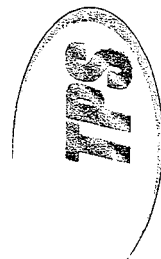
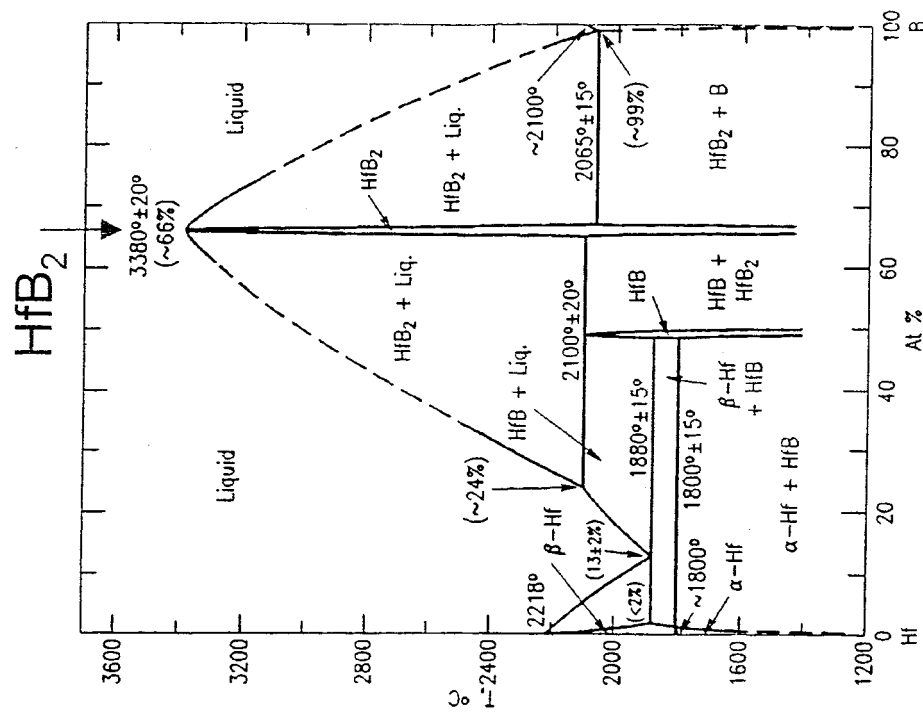
HfB₂-SiC

HfB₂

- HfB₂ has a narrow range of stoichiometry with a melting temperature of 3380°C
- Density = 11.2 g/cc

SiC

- aids densification
- limits grain growth
- may enhance oxidation resistance
- Density = 3.2 g/cc



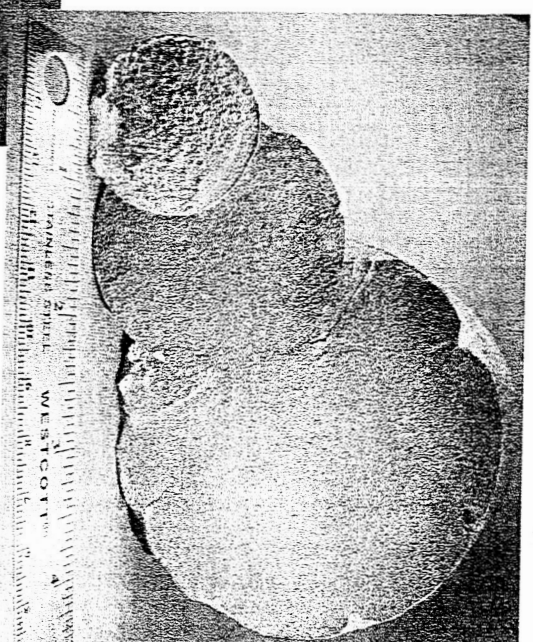
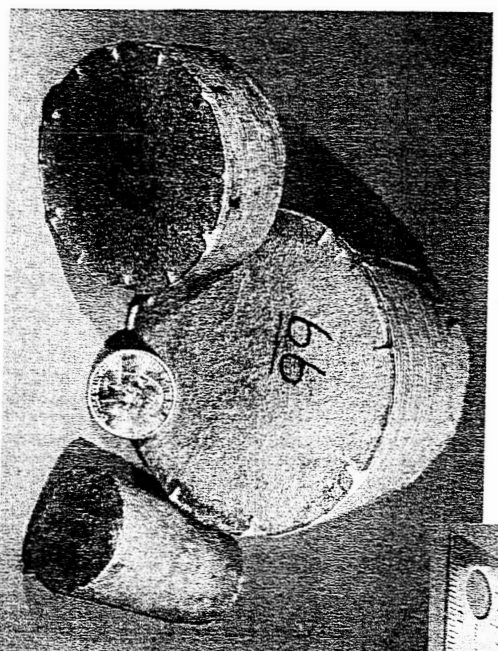


Hot Pressing



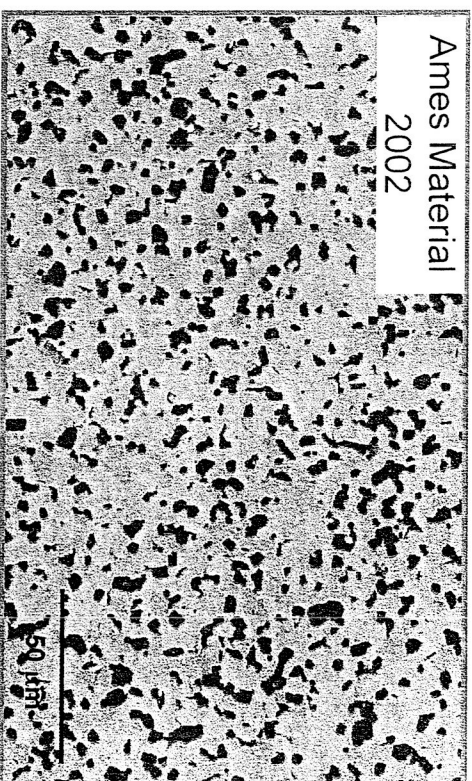
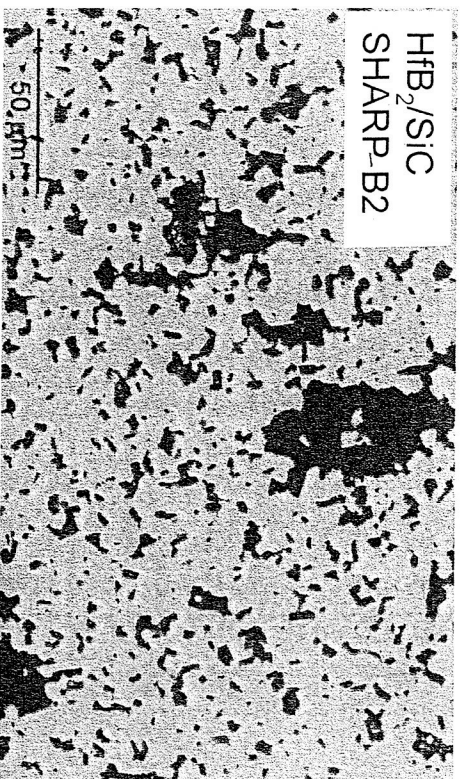
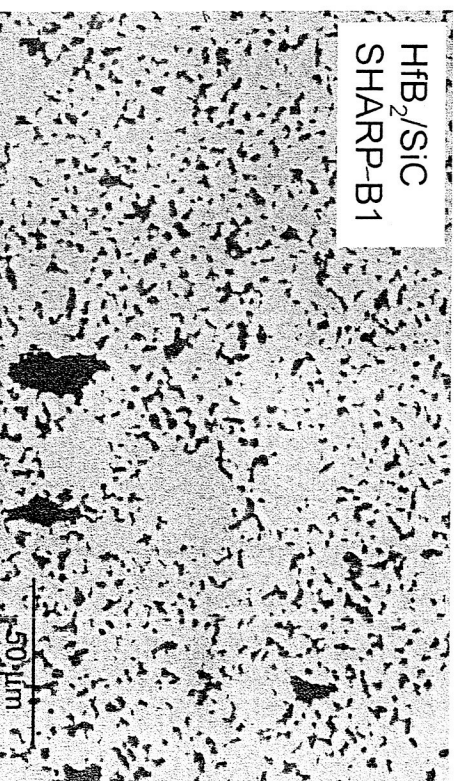
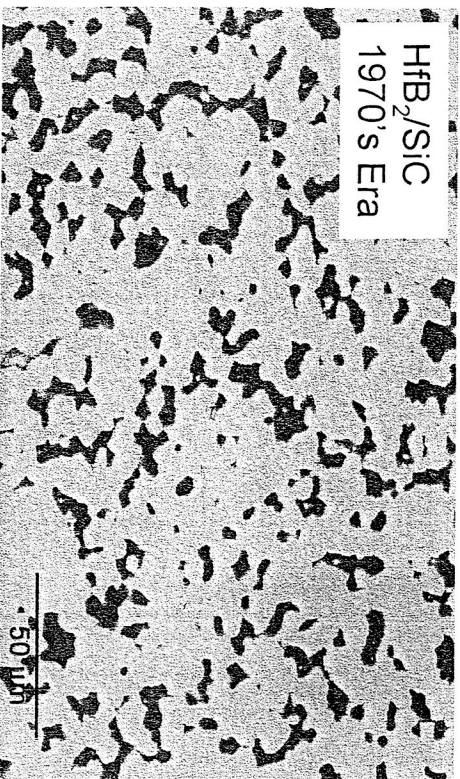
- Granulated powders are loaded into grafoil lined graphite dies
- Hot press has a graphite element with graphite insulation.
- Typical hot pressing parameters:
 - Atmosphere
 - Initially vacuum
 - Switch to inert (Ar or He) at 2000°C
 - Extends graphite element life.
 - Temperatures
 - 2000°C to 2200°C
 - Pressures
 - 3 to 4 ksi
- 67 billets pressed to date
 - (8) 2" dia. x 2" tall billets
 - (1) 3" dia. x 2" tall billet

maxing





Improved Powder Handling Results In More Uniform UHTC Microstructures

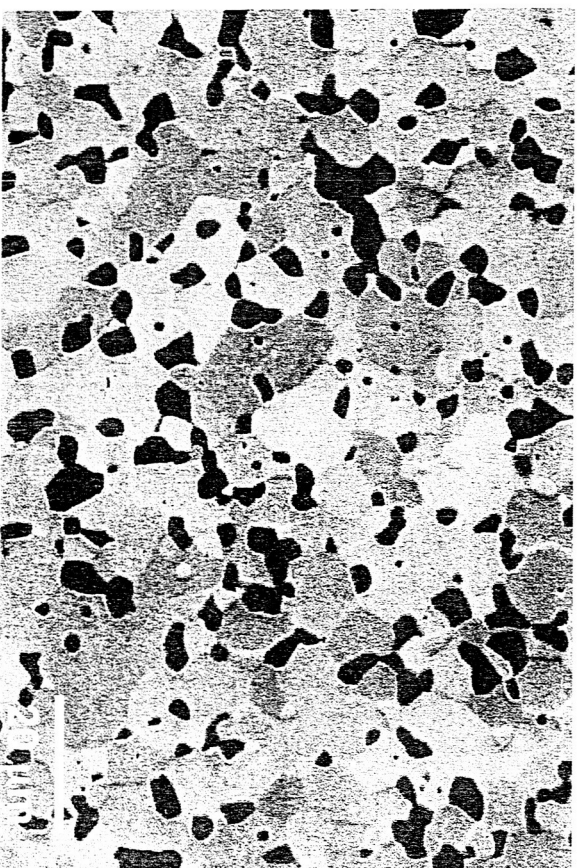
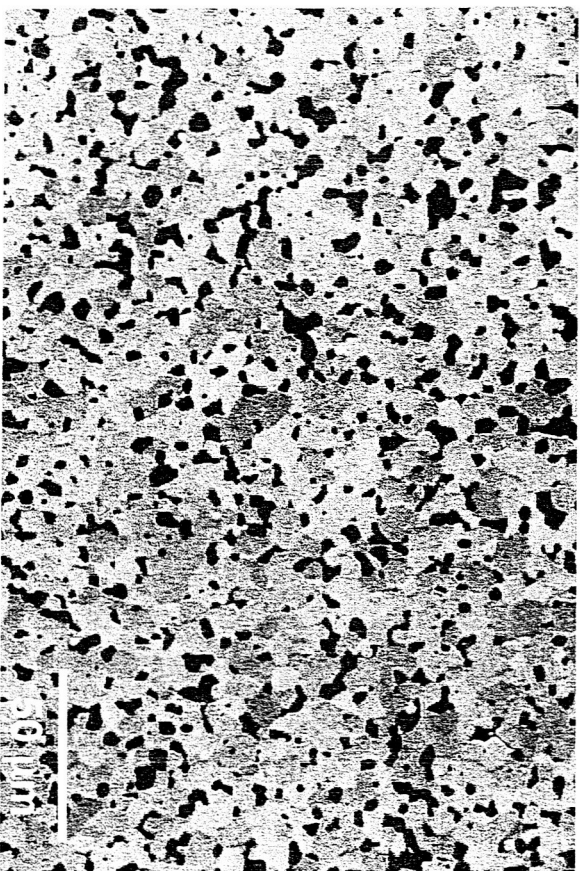


- Improved powder handling eliminates SiC and HfB₂ agglomeration common in previous materials.





Microstructures of Current HfB₂-SiC Materials

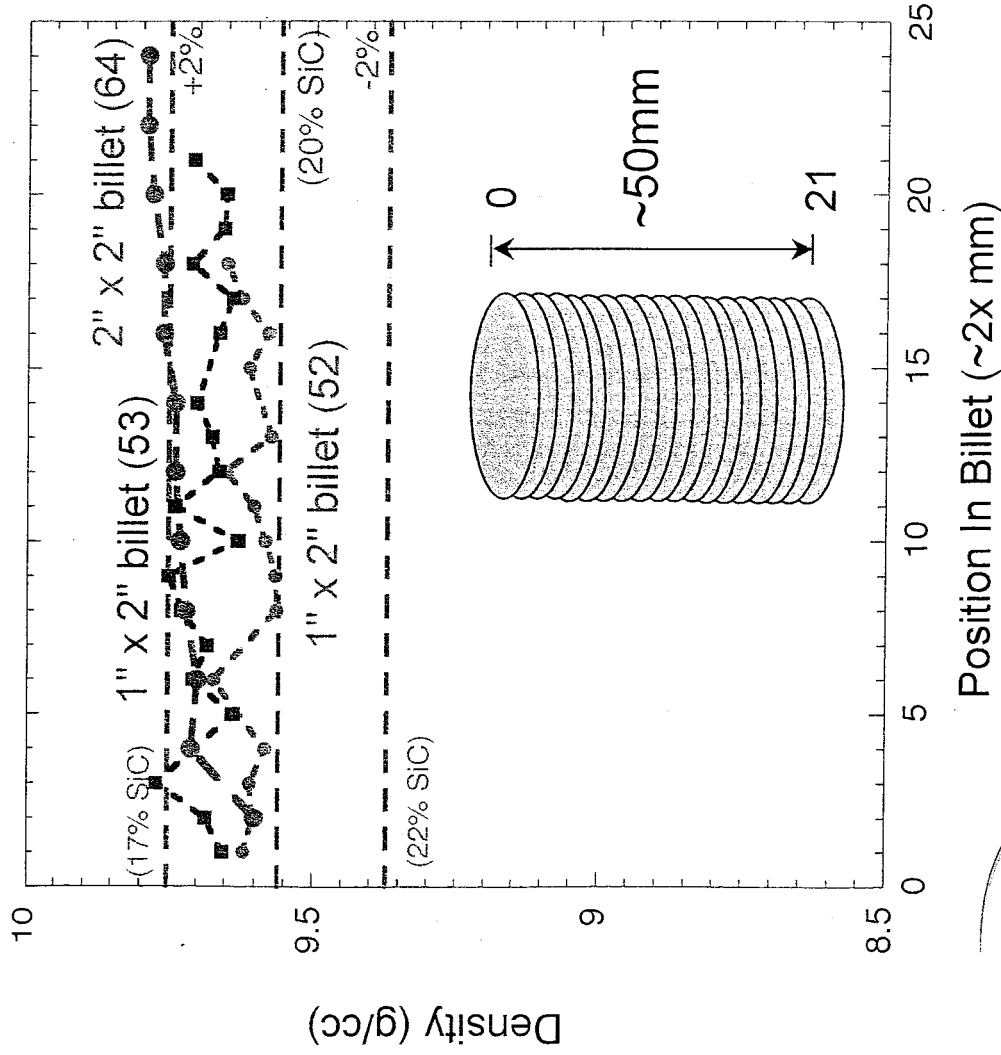


- Microstructures show uniform distribution of SiC with a relatively fine grain size.
- XRD and EDS spectra do not reveal the presence of oxide containing phases

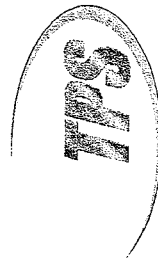




2" Diameter Billet Has a Slightly Larger Density Gradient than the 1" Diameter Billets

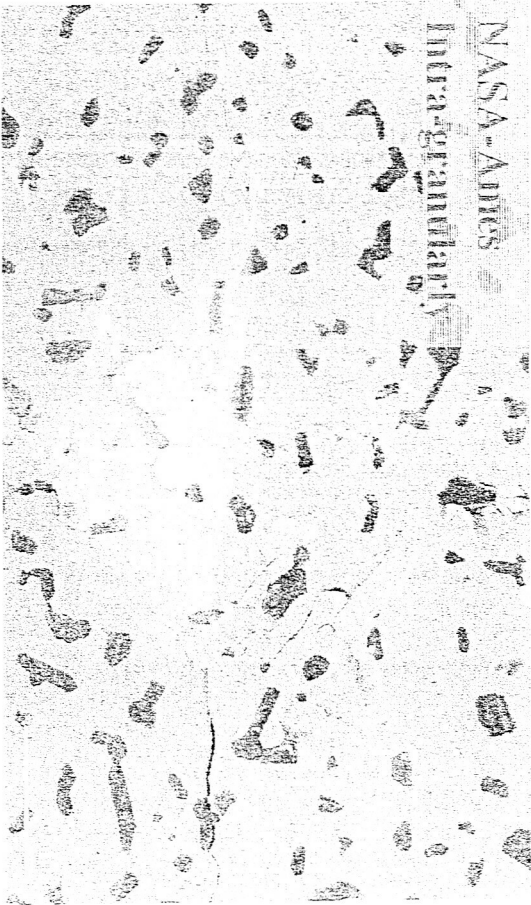
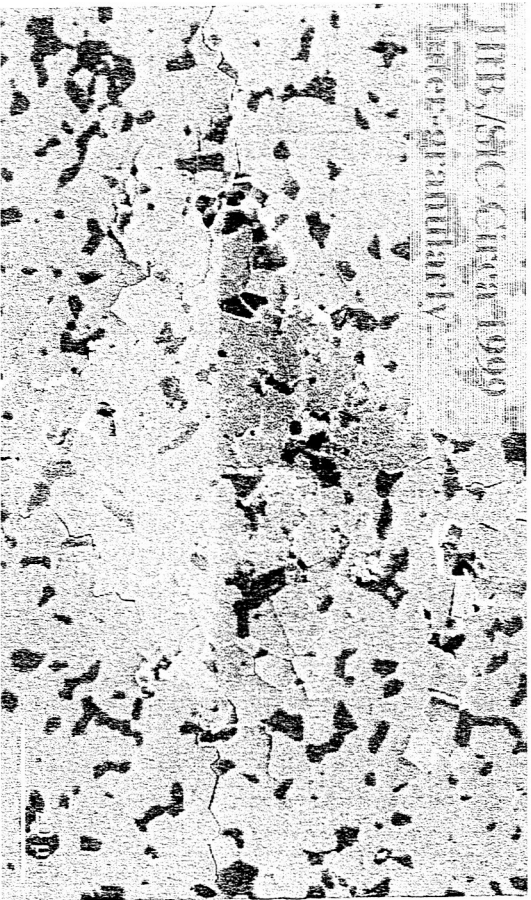


- Hot pressing schedule has not been optimized for billet scale-up.
- Densities are typically higher than theoretical due to loss of SiC during hot pressing.
- Die packing currently performed by hand, likely to result in density gradients within the powder during die packing
- Iso-static pressing of the powder, prior to die packing should increase density uniformity within powder pack increasing final hot pressed density uniformity and we should have this capability soon.





Previous HfB₂/SiC Materials and Ames HfB₂/SiC Have Comparable Hardness



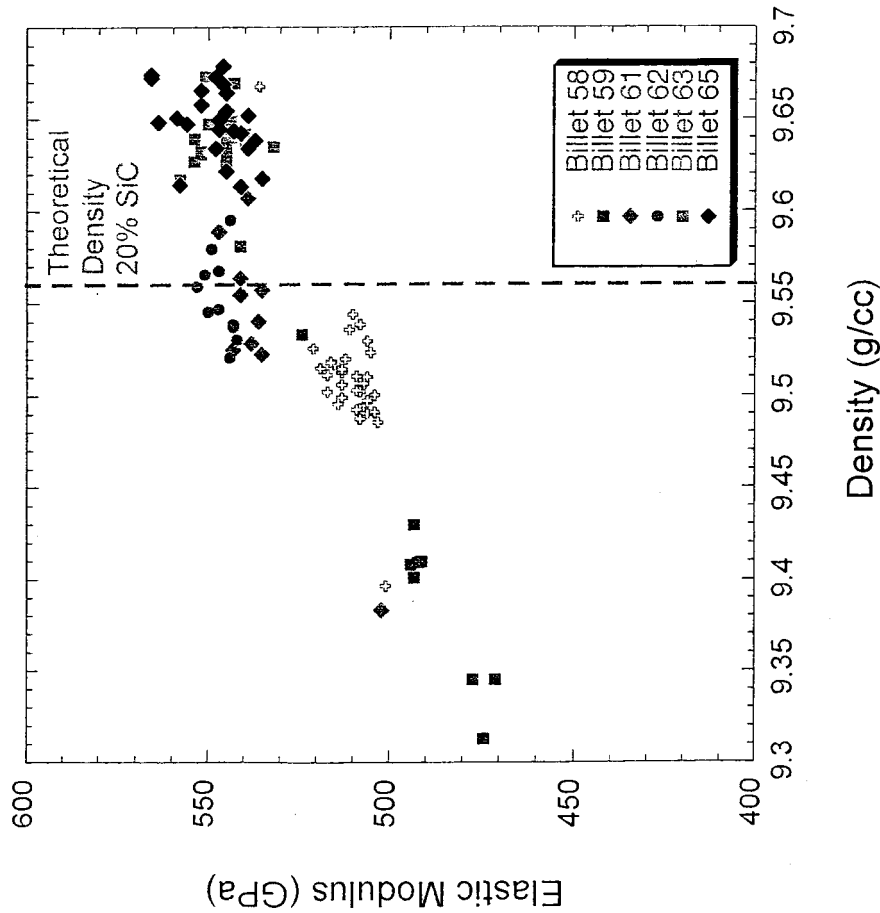
Sample ID	Vickers Hardness(GPa)	Standard Deviation
Ames Material	19.9	0.9
Circa 1999	21.2	1.0

- Cracks from indent in Ames material propagate intra-granularly (through the grains) where as in the heritage materials cracks propagated inter-granularly (between the grains).



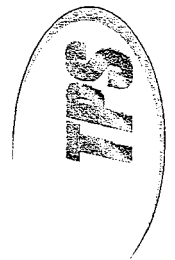


Recent Billets Have Consistent Elastic Moduli



Billet #	Elastic Modulus (GPa)	# of Bars Tested
58	510 ± 9	37
59	490 ± 17	9
61	536 ± 10	10
62	547 ± 4	11
63	546 ± 6	19
65	549 ± 9	24

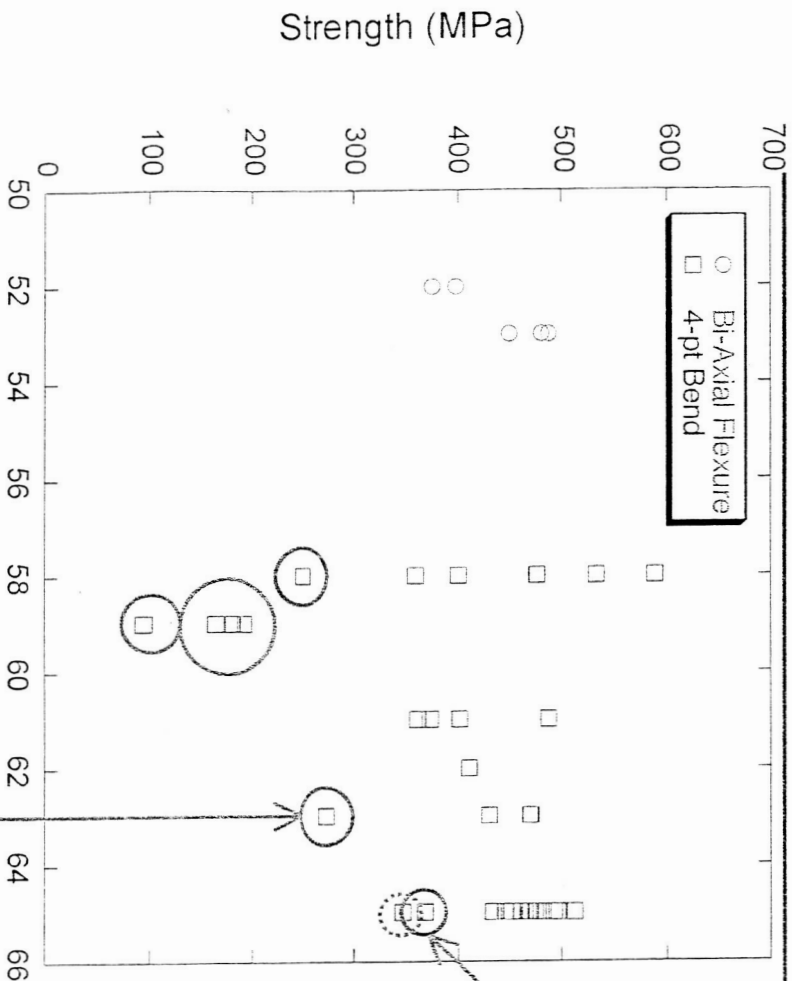
- Modulus decreases with decrease in density
- Decreased moduli probably due to a combination of porosity and change in SiC content (↑ SiC)
- Modulus measured using a pulse echo technique



Washburn
Smallman



Improved Processing Reduces Strength Distribution in Later Billets



Large Grafoil Flake at chamfered edge

Strength measured in 4-pt bending
Bar Size: 3 x 4 x 45 mm

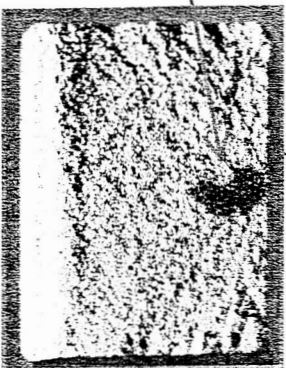
Bi-axial testing
Disc Size: 25mm dia. x 1mm thick

As ground surfaces

○ Extrinsic Defects

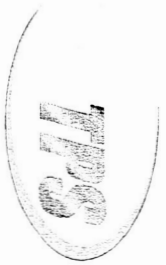
Billet #

Large Grafoil Flake



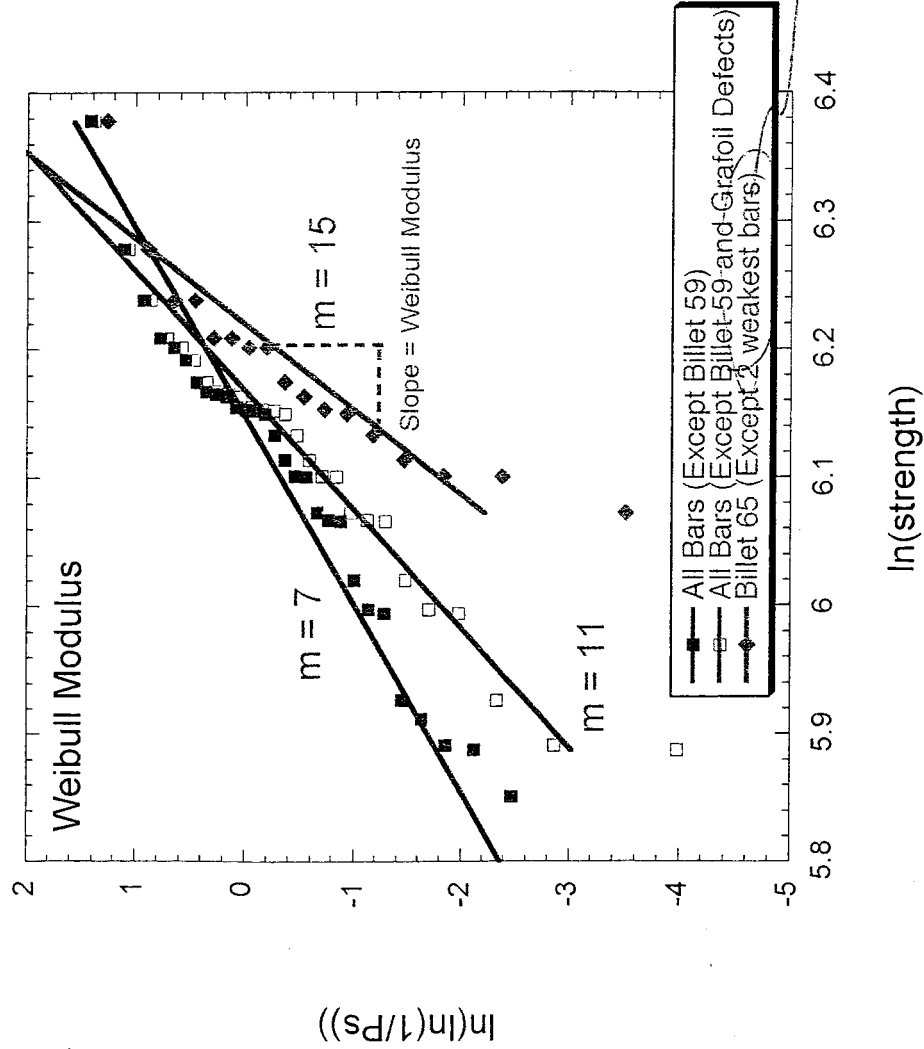
- Grafoil flakes introduced into billets during hand packing
- Flakes are responsible for low strengths in billet #59
- Improved die packing will eliminate this source of extrinsic defects

ASTM C1161



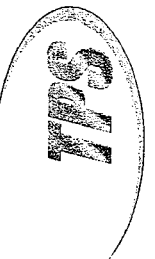


Weibull Modulus of ARC HfB₂/SiC Improved Compared to Previous Materials



- Strength distributions are improving with time, as experience is gained.

HDW many samples?



Weibull Modulus of previous materials (1999 era) ~4.

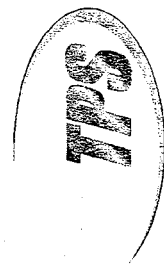


Summary of Strengths

Billet #	Strength (MPa)	# of Bars Tested	Strength Less Extrinsic Defects (MPa)
58	440 ± 114	7	473 ± 89 (6)
59	157 ± 43	4	
61	407 ± 57	4	
62	411	0	
63	415 ± 81	5	451 ± 22 (4)
65	454 ± 46	14	460 ± 41 (13) 470 ± 23 (12)*
SHARP-B2	356 ± 91	30	
ManLabs	312 ± 26	3	

• For this average and standard deviation assumed that both low strength bars in billet 65 had an extrinsic defect such as grafoil[®], fractography has confirmed this for one bar, continuing examination of other bars.

• All strengths measured in 4-pt bending on 3 x 4 x 45 mm bars

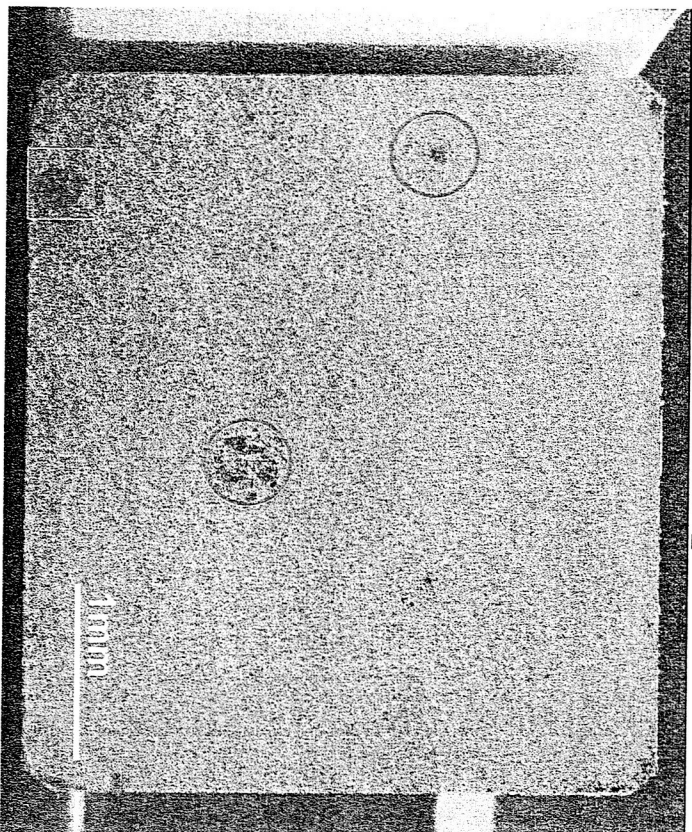




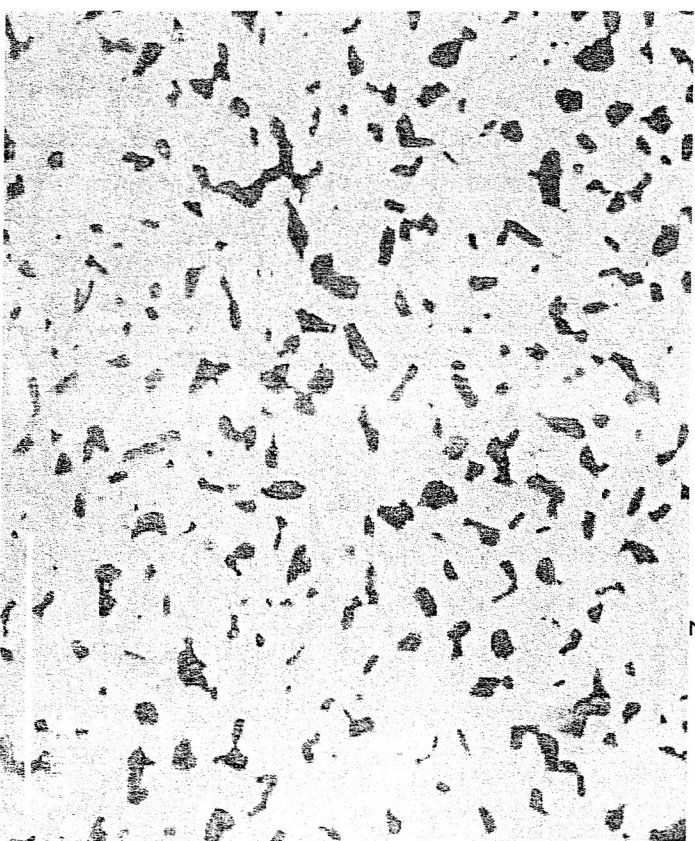
Fracture Surfaces of ARC Materials Do Not Show Evidence of SiC Agglomeration

A
Ames Research Center

Circa 1999 HfB₂/SiC



Ames Processed HfB₂/SiC



which

samples? more, from 1999 data

- Red circles highlight SiC agglomerates found in SHARP-B2 material as a result of un-optimized powder processing
- Fracture surfaces of ARC materials do not reveal SiC agglomeration
- Some ARC bars show Grafoil flakes in the material introduced during die packing
 - Grafoil defects can be eliminated via improved die packing procedures

1130

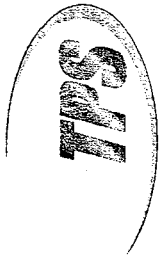
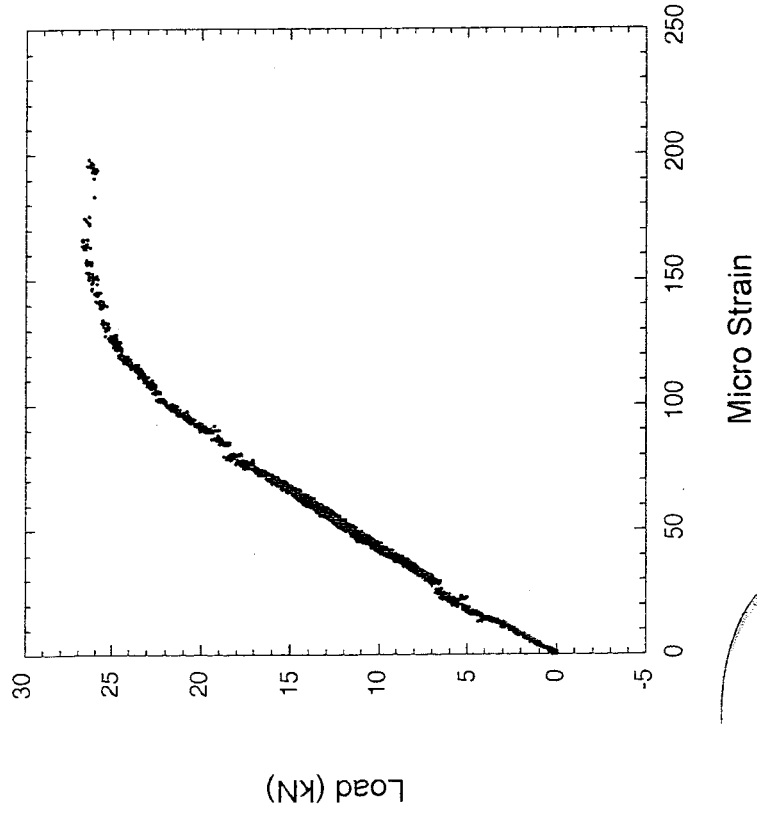


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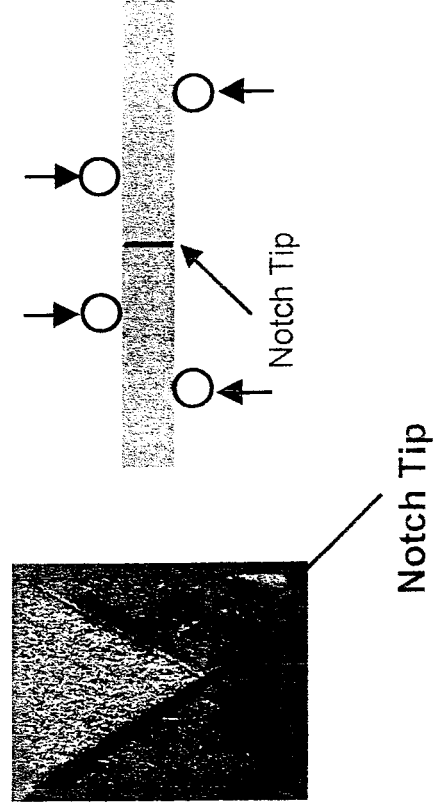
SiC Particulate Does Not Appear to Effect the Materials Fracture Toughness



- Fracture toughness measured according to ASTM C1421
- Used Chevron Notched Specimens
- Bar Size: 3 x 4 x 45 mm
- Need stable crack growth during test

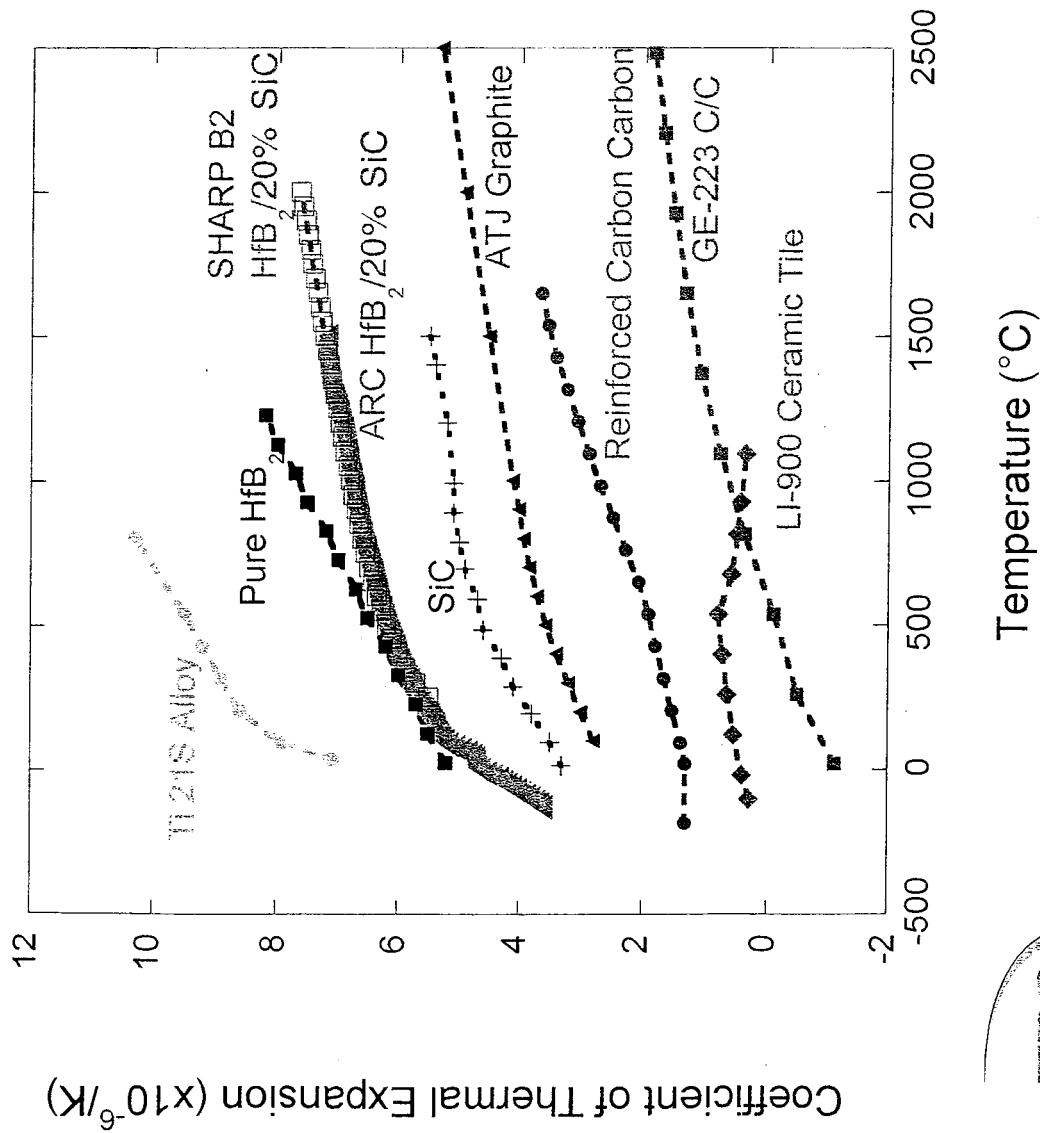


Material	K_{IVB} (MPa $m^{1/2}$)
Si ₃ N ₄	3 - 7
Al ₂ O ₃	3 - 4
SiC	3 - 4
Porcelain	~1
Si	~1
HfB ₂ /20% SiC	4.1 ± 0.2

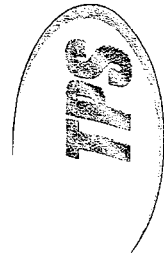




CTE of ARC HfB_2/SiC is the Same as SHARP-B2 Material

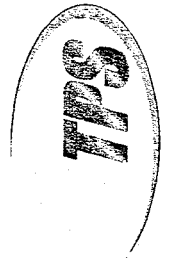
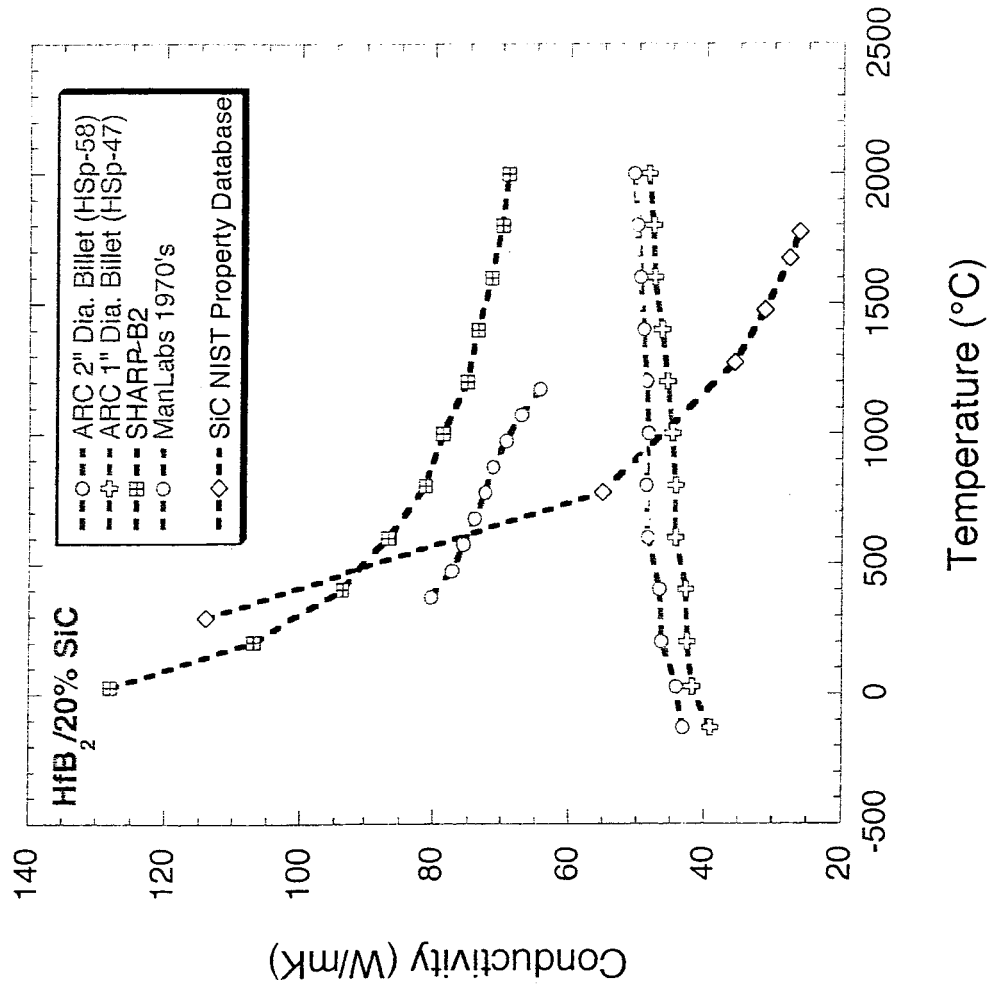


- CTE measured using high temperature dilatometry
- Pushrod dilatometer used
- $T = -130^{\circ}\text{C}$ to 1500°C





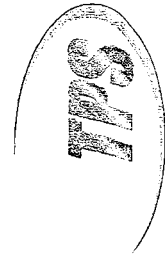
Conductivity of ARC Materials Lower than Heritage Materials





Summary

- Modified hot pressing schedule has significantly improved UHTC billet processing
 - Density and microstructure uniformity have improved
- 2" dia. x 2" tall UHTC billets have been successfully hot pressed
 - Scaled up billets have slightly higher density gradients axially than 1" billets
 - Need to evaluate radial density uniformity
 - Hot press schedule has not been optimized for scaled up billets
 - Hot pressed (1) 3" dia. x 2" tall billet
- Strengths and strength distributions are improving with experience
 - Need to evaluate strength uniformity in the center of the billets
 - Most bars cut from outside of billet around wedge models
- CTE or ARC materials compares favorably with heritage materials.
- Thermal conductivity of ARC materials considerably different than that of heritage materials.



(6) 4/5/05
F